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GTS-1: A CERTIFIED REFERENCE GOLD TAILINGS SAMPLE

H.F. Steger and W.S. Bowman

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GTS-1: A CERTIFIED REFERENCE GOLD TAILINGS SAMPLE

by

H.F. Steger* and W.S. Bowman**

SYNOPSIS

A 295-kg composite sample of gold tailings from Kirkland Lake and South Porcupine, Ontario, was prepared as a compositional reference material. GTS-1 was passed through a 74 µm screen, blended in one lot and bottled in 400-g units. Its homogeneity was confirmed by a combined fire assay-atomic absorption procedure for gold.

In a "free choice" analytical program, 22 laboratories contributed results for gold in one bottle of GTS-1. Based on a statistical analysis of the data, a recommended value was assigned for Au at 0.346 µg/g or 0.0101 oz/ton.

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Note: Major contributions were also made by other staff members of the Mineral Sciences Laboratories.

GTS-1: ÉCHANTILLON DE RÉFÉRENCE DES RÉSIDUS D'OR

par

H.F. Steger* et W.S. Bauman**

SYNOPSIS

Un échantillon mixte de 295 kg de résidus d'or provenant de Kirkland Lake et de South Porcupine en Ontario à été préparé comme matériau de référence de composition. Le GTS-1 a été tamisé à une granulométrie de moins 74 µm, mélangé en lot de minerai et embouteillé en unités de 400 g. L'homogénéité de GTS-1 a été confirmée quant à l'or par une méthode analytique qui combine des techniques pyrognostiques et d'absorption atomique.

En vertu d'un programme analytique de "libre choix", 22 laboratoires ont fourni des résultats sur la teneur en or d'un flacon de GTS-1. L'analyse statistique des donnés fut utilisée pour attribuer une valeur recommandée de 0,346 µg/g ou 0,0101 oz/tonne à l'or.

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Nota: Ce travail à été fait en collaboration avec d'autres employés des Laboratoires des sciences minérales.

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INTRODUCTION

The preparation, characterization and certification of gold tailings GTS-1 is a further contribution by the Canadian Certified Reference Materials Project (CCRMP) in its endeavour to provide compositional reference ores, concentrates and related products typical of Canadian deposits and generally unavailable from other sources for use in analytical laboratories associated with mining, metallurgy and the earth sciences. Other reference materials certified by CCRMP are described in a catalogue available from CANMET, Energy, Mines and Resources Canada, Ottawa (1).

GTS-1 was chosen for preparation in response to requests for reference materials of relatively simple siliceous matrix with gold content. An interlaboratory program was conducted to obtain results for gold from 22 commercial, industrial and government laboratories using analytical methods of their choice. The results should therefore be indicative of the practical "state-of-the-art" of the analysis for gold.

NATURE AND PREPARATION

GTS-1 is a composite of mill tailings donated by Lac Minerals of Kirkland Lake in July 1982 and by Dome Mines Limited of South Porcupine, Ontario in September 1982.

The ore at the Macassa Division of Lac Minerals consists of quartz veins, carbonated, silicified and pyritized syenite, porphory syenite and augite syenite enclosed in fissure-type veins, stockworks and vein breccias (2). It is crushed to 96-98% minus 45 μm and treated with sodium cyanide. The gangue is filtered off and disposed as tailings.

The ore at Dome Mines Limited consists of gold in quartz and ankerite with pyrite and pyrrhotite present to the the extent of about 2.5%. Host rocks are intermediate greenstone, conglomerate, slate and porphory (3). The ore is wet-ground and treated with cyanide.

The tailings samples from the two locations were passed through a 74 μm screen and blended in separate batches. Approximately 179 kg of the tailings sample from Lac Minerals and 116 kg of that from Dome Mines Limited were tumbled in a 570-L blender for 15 h and bottled in 400-g units. GTS-1 was found to be sufficiently homogeneous for gold by a combined fire assay-atomic absorption spectrometric procedure to qualify as a reference material. Results of the confirmation of the homogeneity of GTS-1 are summarized in Appendix A.

The approximate chemical composition and particle size analysis are given in Tables 1 and 2.

Table 1 - Approximate chemical composition of GTS -1

Element	wt %[a]
Si	23.4
Al	6.4
K	3.1
Fe	6.0
Ca	3.9
Na	1.4
C (Total)	2.1
S	1.1
L.O.I.	7.0
H_2O (105°C)	0.12

[a]Mean of duplicate determinations

Table 2 - Particle size analysis of GTS-1 (wet screen)

Size of fraction (μm)	wt %[a]
-104 + 74	0.1
- 74 + 55	7.1
- 55 + 37	8.0
- 37	84.8

[a]Mean of duplicate determinations

INTERLABORATORY PROGRAM FOR CERTIFICATION

Participating laboratories in the certification program for GTS-1 are listed alphabetically in Appendix B. Each was assigned a code number which bears no relation to its alphabetical order.

Each laboratory was requested to contribute five replicate results for gold on one bottle of GTS-1 by a method of its choice and to report the results on an "as is" basis. Some laboratories, however, deviated from the request for five results or contributed results by more than one method. In the latter instance, each set was considered statistically independent.

The results of CANMET's assessment of the homogeneity of GTS-1 were included in the program. However, to avoid any biasing of the statistics, only five results, chosen at random out of the 45 available, were used in subsequent calculations. The recommended value for gold is given in Table 3. Methodological and analytical information is presented in Tables 4 and 5.

Table 3 - Recommended value and associated statistical parameters for gold in GTS-1

No. of laboratories	22
No. of results	193
Mean	0.346 µg/g , 0.0101 oz/ton
95% confidence limits,	
low	0.330 µg/g , 0.0096 oz/ton
high	0.362 µg/g , 0.0106 oz/ton
σ_A*	0.017 µg/g

*Average within-laboratory standard deviation

Table 4 - Summary of analytical methods for gold

Method	Decomposition, separation, etc.	Laboratory	n	$\bar{x}$ (µg/g)
Fire assay - atomic absorption	Lead button collection; dissolution in HNO_3 + HCl	CANMET, 5a	10	0.34
	Silver added to fusion; lead button collection; cupellation to silver bead; silver parted with HNO_3; gold dissolution in aqua regia	2,4,6,7,8,9 10,11,12,13, 16b, 18,19,20	97	0.36
	Silver added to fusion; lead button collection; cupellation to silver bead; dissolution in aqua regia; gold extracted into MIBK	14a, 15	15	0.40
Fire assay - emission spectrometry	Silver added to fusion; lead button collection; cupellation to silver bead; dissolution in aqua regia	5b	5	0.31
Fire assay - DCP emission spectrometry	Silver added to fusion; lead button collection; cupellation to silver bead; dissolution in aqua regia	3a, 17c	14	0.31
Fire assay - ICP emission spectrometry	Silver added to fusion; lead button collection; cupellation to silver bead; dissolution in aqua regia	21	5	0.32

Table 4 - Summary of analytical methods for gold (Cont'd)

Method	Decomposition, separation, etc.	Laboratory	n	$\bar{x}$ (μg/g)
Fire assay - neutron activation analysis	Silver added to fusion; lead button collection; cupellation to silver bead	3b, 16a, 17b	26	0.31
Atomic absorption	Dissolution in aqua regia; gold extracted into MIBK	14b	5	0.37
Colorimetry	Roasted at 500°C; dissolution in HNO_3 + HCl + HF + Br_2; gold extracted into toluene as trioctylamine-bromide complex; gold determined in organic phase after treatment with Thio-Michler's ketone complex [I. Tsukahara, Talanta 24 (1977): 633]	1	5	0.27
Instrumental neutron activation analysis	Sample irradiated directly	17a	11	0.37

Table 5 - Analytical results, laboratory means and standard deviations for gold

REFERENCE MATERIAL GTS-1

GOLD UG/G

						MEAN	S.D.
CANMET (FA-AA)	0.336	0.350	0.360	0.360	0.350	.3512	.0099
LAB- 1 (CHLOR)	0.276	0.264	0.264	0.270	0.251	.2644	.0109
LAB- 2 (FA-AA)	0.373	0.396	0.390	0.333	0.347	.3678	.0176
LAB- 3 (FA-DCP)	0.300	0.270	0.310	0.330	0.300	.3100	.0233
	0.310	0.290	0.310				
LAB- 3 (FA-HAA)	0.290	0.260	0.290	0.280	0.320	.2860	.0217
	0.300	0.270	0.290	0.290	0.310		
LAB- 4 (FA-AA)	0.360	0.370	0.364	0.360	0.370	.3714	.0060
	0.380	0.364	0.364	0.372	0.376		
	0.380	0.360	0.370	0.364	0.382		
	0.370						
LAB- 5 (FA-AA)	0.327	0.339	0.320	0.335	0.343	.3336	.0069
LAB- 5 (FA-ES)	0.32	0.31	0.31	0.31	0.29	.3060	.0152
LAB- 6 (FA-AA)	0.360	0.362	0.354	0.360	0.359	.3606	.0031
LAB- 7 (FA-AA)	0.400	0.422	0.422	0.409	0.427	.4163	.0083
	0.410						
LAB- 8 (FA-AA)	0.40	0.41	0.39	0.42	0.39	.4120	.0249
LAB- 9 (FA-AA)	0.4119	0.3772	0.3772	0.4081	0.3772	.4046	.0447
LAB-10 (FA-AA)	0.330	0.309	0.306	0.329	0.314	.3432	.0276
LAB-10 (FA-AA)	0.329	0.323	0.305	0.329	0.309	.3332	.0290
LAB-10 (FA-AA)	0.302	0.348	0.303	0.336	0.343	.3424	.0230
LAB-11 (FA-AA)	0.305	0.296	0.300	0.293	0.292	.2972	.0054
LAB-11 (FA-AA)	0.290	0.296	0.315	0.291	0.296	.2976	.0101
LAB-12 (FA-AA)	0.36	0.40	0.36	0.36	0.40	.3760	.0219
LAB-13 (FA-AA)	0.330	0.333	0.330	0.324	0.329	.3324	.0060
LAB-14 (FA-AA)	0.377	0.360	0.395	0.377	0.377	.3772	.0124
LAB-14 (AA)	0.377	0.377	0.360	0.360	0.377	.3702	.0093
LAB-15 (FA-AA)	0.444	0.460	0.463	0.393	0.412	.4092	.0681
	0.366	0.273	0.444	0.393	0.490		
LAB-16 (FA-HAA)	0.321	0.301	0.324	0.340	0.332	.3292	.0196
	0.331	0.310	0.303	0.300	0.301		
LAB-16 (FA-AA)	0.290	0.300	0.330	0.290	0.290	.3000	.0173
LAB-17 (NAA)	0.413	0.370	0.350	0.386	0.373	.3727	.0211
	0.361	0.396	0.344	0.354	0.301		
	0.352						
LAB-17 (FA-HAA)	0.310	0.330	0.300	0.330	0.330	.3230	.0176
	0.330						
LAB-17 (FA-DCP)	0.310	0.310	0.310	0.310	0.300	.3083	.0041
	0.310						
LAB-18 (FA-AA)	0.39	0.39	0.42	0.42	0.42	.4080	.0164
LAB-19 (FA-AA)	0.309	0.296	0.302	0.313	0.322	.3060	.0103
LAB-20 (FA-AA)	0.370	0.397	0.397	0.370	0.370	.3640	.0071
LAB-21 (FA-DCP)	0.37	0.32	0.31	0.30	0.32	.3240	.0270

STATISTICAL TREATMENT OF ANALYTICAL RESULTS

DETECTION OF OUTLIERS

There were no physical or statistical outliers detected for GTS-1.

ESTIMATION OF CONSENSUS VALUE AND 95% CONFIDENCE LIMITS

A one-way analysis of variance technique was used to estimate the consensus value and its variance. This approach considers the results of the described certification program to be only one sampling out of a universal set of results. The analytical data were assumed to fit the model (4).

$$x_{ij} = \mu + y_i + e_{ij}$$

where x_{ij} = the j^{th} result in set i,
μ = the true consensus value,
y_i = the discrepancy between the mean of the results in set i ($\bar{x}_{i\cdot}$) and μ, and
e_{ij} = the discrepancy between x_{ij} and $\bar{x}_{i\cdot}$.

It is assumed that both y_i and e_{ij} are normally distributed with means of zero and variance of w^2 and σ^2, respectively. The significance of w^2 is detected by comparing the ratio of between-set mean squares with within-set mean squares with the F statistic at the 95% confidence level and with the appropriate degrees of freedom.

The consensus value of the assumed model is estimated by the overall mean $\bar{x}_{\cdot\cdot}$:

$$\bar{x}_{\cdot\cdot} = \sum_{i}^{k}\sum_{j}^{n_i} x_{ij} \Big/ \sum_{i}^{k} n_i$$

where n_i = the number of results in set i and
k = the number of sets.

The value of σ^2 is estimated by s_1^2 which is given by

$$s_1^2 = \sum_{i}^{k}\sum_{j}^{n_i} (x_{ij} - \bar{x}_{i\cdot})^2 \Big/ \left(\sum_{i}^{k} n_i - k\right)$$

The value of w^2 is estimated by

$$w^2 = (s_2^2 - s_1^2) \Big/ \frac{1}{k-1}\left(\sum_{i}^{k} n_i - \sum_{i}^{k} n_i^2 \Big/ \sum_{i}^{k} n_i\right)$$

where

$$s_2^2 = \sum_{i}^{k} n_i (\bar{x}_{i\cdot} - \bar{x}_{\cdot\cdot})^2 \Big/ k - 1$$

The variance of the overall mean is given by

$$v[\bar{x}_{\cdot\cdot}] = \left(\sum_{i}^{k} n_i^2 \Big/ \left(\sum_{i}^{k} n_i\right)^2\right) w^2 + \left(1 \Big/ \sum_{i}^{k} n_i\right) \sigma^2$$

and the 95% confidence limits for $\bar{x}_{\cdot\cdot}$ are

$$\bar{x}_{\cdot\cdot} \pm t_{0.975,\,(k-1)} \sqrt{v[\bar{x}_{\cdot\cdot}]}$$

It should be noted that 95% confidence limits denote that if the certification program were performed 100 times, the overall mean in 95 would fall within the prescribed limits.

The average within-set standard deviation, σ_A, is a measure of the average within-bottle precision as determined by the analytical methods used. The implication exists therefore that a laboratory using a method of average or better reproducibility should obtain individual results for a given certified element with a precison that is at least comparable to the reported value of σ_A.

CRITERION FOR CERTIFICATION

The ratio of the between-laboratory to the within-laboratory standard deviation, σ_B/σ_A, where

$$\sigma_B = \sqrt{\left[\sum_{i}^{k}\left(\bar{x}_{i\cdot} - \left(\sum_{i}^{k} \bar{x}_{i\cdot}\right)/k\right)\right]^2 \Big/ k-1}$$

is a measure of the quality of the certification data for the reference materials of CCMMP (5).

The acceptable upper limit for σ_B/σ_A is 3 for all elements except uranium for which an upper limit of 2 is more realistic.

The criterion for the certification of an element in a reference material is RP, the percentage of sets of results that must be rejected to give a value of σ_B/σ_A equal to or less than the acceptable upper limit. RP should not exceed 15%.

For GTS-1, a value of 2.31 for σ_B/σ_A was obtained for all results. Therefore, RP = 0% and this reference material can be certified for its gold content.

DISCUSSION

Table 4 is a summary of a methodological classification of accepted analytical results where there is a clear-cut distinction between types of methods in decomposition, separations and determination steps. As expected, pre-concentration of gold was in most cases performed by a fire assay fusion after the addition of silver. An atomic absorption finish was most frequently used.

Figure 1 illustrates the plot of the relative frequency against the gold interval for all results. The distribution observed shows the consensus attained by the participating laboratories.

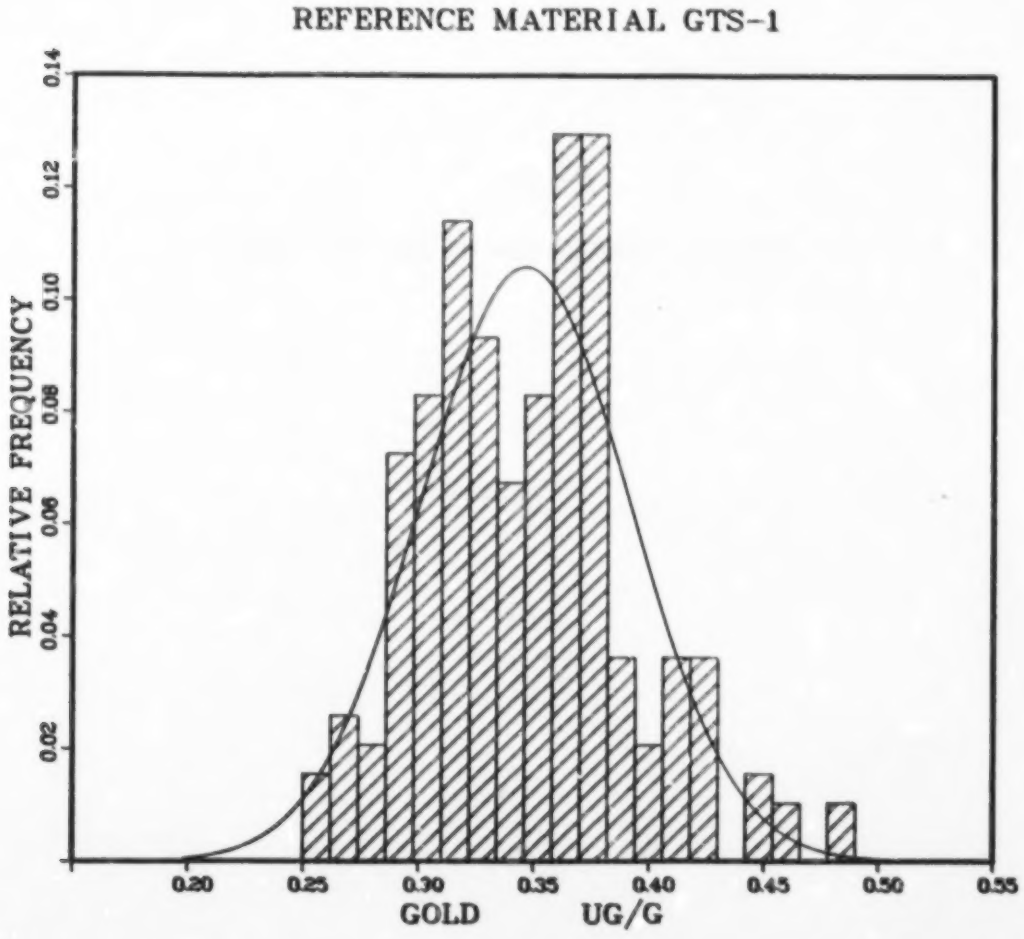

Fig. 1 - Histogram for gold results

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APPENDIX A

CONFIRMATION OF HOMOGENEITY OF GTS-1

The homogeneity of GTS-1 was confirmed at CANMET by analyzing 15 bottles for gold in triplicate using a combined fire assay-atomic absorption procedure (5). These bottles were selected as follows. The stock of 720 bottles was divided into 15 lots of 48 bottles. The code numbers of the first bottle were selected at random out of the first lot. The code numbers of the other 14 bottles were given as the code number of the preceding bottle plus 48. The results of the analysis are shown in Table 6.

A one-way analysis of variance technique was used to assess the homogeneity (4). Herein, the ratio of the between-bottle to within-bottle mean square is compared with the F statistic at the 95% level of probability. No evidence of bottle-to-bottle inhomogeneity was found for gold.

Table 6 - Confirmation of homogeneity of GTS-1

	Au µg/g			
Bottle	Individual			Mean
25	.370	.340	.350	0.353
73	.360	.336	.380	0.359
121	.340	.380	.370	0.363
169	.370	.372	.350	0.364
217	.340	.336	.340	0.339
265	.340	.350	.350	0.347
313	.350	.370	.380	0.367
361	.340	.390	.360	0.363
409	.370	.370	.370	0.370
457	.350	.346	.370	0.355
505	.360	.350	.350	0.353
553	.350	.380	.360	0.363
601	.350	.360	.350	0.353
649	.350	.340	.340	0.343
697	.360	.340	.350	0.350

Overall mean is 0.356

Table 6 - Cont'd

Analysis of variance table for gold

Source of variation	Degrees of freedom	Mean square
Between bottles	14	2.458×10^{-4}
Within bottles	30	1.869×10^{-4}
Total	44	

Calculated F statistic = 1.315

F.95 (14, 30) = 2.0374

Null hypothesis of no difference between bottles is accepted.

APPENDIX B

PARTICIPATING LABORATORIES

Atlantic Analytical Services Ltd.
St. John, New Brunswick
A. Graham

Assayer's (Ontario) Ltd.
Toronto, Ontario
J. van Engelen

Bondar-Clegg and Company Ltd.
North Vancouver, British Columbia
R.K. Rogers

Bondar-Clegg and Company Ltd.
Ottawa, Ontario
P. Haulena

CANMET, Energy, Mines and Resources Canada
Mineral Sciences Laboratories
Ottawa, Ontario.

Chemex Labs. Ltd.
North Vancouver, British Columbia
B.L. Twaites

Chemex Labs. (Alberta) Ltd.
Calgary, Alberta
R.B. Pang

Dome Mines Limited, Assay Office
South Porcupine, Ontario
W. Clifford

Falconbridge Nickel Mines Ltd.
Metallurgical Laboratories
Thornhill, Ontario
J.R. Johnston

Hudson Bay Mining and Smelting Company Ltd.
Flin Flon, Manitoba
D. Allen

INCO Ltd.
J. Roy Gordon Research Laboratory
Sheridan Park, Ontario
St.J.H. Blakely

INCO Metals Ltd.
Copper Cliff, Ontario
J. Bozic

Kamloops Research and Assay Laboratory Ltd.
Kamloops, British Columbia
D.A. Blundell

Lakefield Research of Canada Ltd.
Lakefield, Ontario
A.E. Carr

Metriclab (1980) Inc.
Ste-Marthe-sur-le-Lac, Quebec
H. Blais

Mintek
Randburg, South Africa
H. Stoch

Nuclear Activation Services Ltd.
Hamilton, Ontario
E.L. Hoffman

Noranda Research Centre
Pointe Claire, Quebec
J.D. Kerbyson

Noranda Mines Ltd.
Horne Smelter Laboratory
Noranda, Quebec
M. Bédard

Ontario Ministry of Natural Resources
Geoscience Laboratories
Toronto, Ontario
C. Riddle

Technical Service Laboratories
Mississauga, Ontario
A.H. Debnam

X-Ray Assay Laboratories Ltd.
Don Mills, Ontario
E.J. Brooker